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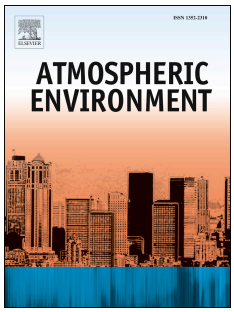

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DETECTION OF BRAKE WEAR AEROSOLS BY AEROSOL TIME-OF-FLIGHT MASS SPECTROMETRY

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HIGHLIGHTS

- Brake wear particles are an important constituent of urban aerosol
- ATOFMS identifies brake dust from Fe and Ba signals
- High laser pulse energies are needed to detect the Ba^+ ion
- Data from several field campaigns are presented

ABSTRACT

Brake dust particles were characterised using an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) operated using two inlet configurations, namely the aerodynamic lens (AFL) inlet and countersunk nozzle inlet. Laboratory studies show that dust particles are characterised by mass spectra containing ions deriving from Fe and Ba and although highly correlated to each other, the Fe and Ba signals were mostly detected using the nozzle inlet with relatively high laser desorption energies. When using the AFL, only [^{56}Fe] and [$^{-88}FeO_2$] ions were observed in brake dust spectra generated using lower laser desorption pulse energies, and only above 0.75 mJ was the [^{138}Ba] ion detected. When used with the preferred nozzle inlet configuration, the [$^{-88}FeO_2$] peak was considered to be the more reliable tracer peak, because it is not present in other types of dust (mineral, tyre, Saharan etc). As shown by the comparison with ambient data from a number of locations, the aerodynamic lens is not as efficient in detecting brake wear particles, with less than 1% of sampled particles attributed to brake wear. Five field campaigns within Birmingham (background, roadside (3) and road tunnel) used the nozzle inlet and showed that dust particles (crustal and road) accounted for between 3.1 and 65.9 % of the particles detected, with the remaining particles being made up from varying percentages of other constituents.

Keywords: ATOFMS; single particles; traffic emissions; resuspension; brake dust

1. INTRODUCTION

Both exhaust and non-exhaust emissions are now the focus of air quality research as tightening policies are reducing the contribution of engine exhaust to the total airborne particulate matter budget, such that non-exhaust emissions are becoming more prominent (Lenschow et al., 2001; Harrison et al., 2001; Querol et al., 2004; Boulter et al., 2006). It is recognised that road traffic is frequently a dominant, but mitigatable, source of particulate matter (PM) accounting for 5-80% of airborne concentrations of PM depending on site and location (Pant and Harrison, 2013). In the UK, the Air Quality Expert Group identified non-exhaust primary PM emissions from road transport as a priority area of uncertainty, and stated the need to update and refine the associated methodologies and estimates (AQEG, 2005). Other, international assessments have also highlighted the need for action (Denier van der Gon et al., 2013; Amato et al., 2014)

Non-exhaust emissions arise from mechanical abrasion and corrosion processes leading to particles with a large proportion in the coarse size range. The most important direct emission sources are associated with the wear of tyres, brakes, clutch and road surfaces through abrasion, and vehicle bodywork through corrosion. Compared to tail-pipe emissions, the coarser nature of non-exhaust emissions implies that they are more likely to be deposited onto the road surface and then be resuspended into the atmosphere both due to vehicle-generated turbulence and by action of the wind (Harrison et al., 2001). The common assumption that most of the primary fine particles ($PM_{2.5}$) and the coarse particles ($PM_{2.5-10}$) arise from exhaust and non-exhaust emissions respectively is not well supported by measurement of non-exhaust PM. There is evidence showing that non-exhaust particles contribute to both the fine and the coarse mode (AQEG 2005) implying a need for measurement of both size fractions.

The frictional contact between a brake pad/shoe and disc/drum rotating with the wheel of the vehicle converts the linear motion of the vehicle into thermal energy. Associated with this process is the gradual wear of the contacting components which in turn liberates brake dust. The brake disc/drum is generally fabricated from cast iron and the contact material of the pads/shoes is made from a range of materials (Thorpe and Harrison, 2008). Recent information on the composition of brake pads used in Europe is available from Hulskotte et al. (2014). Major element components on average comprised 23% Fe, 11% Cu, 5% Zn, and 3% Sn as the dominant metals. Non-metal components in the discs were 2-3% Si, 3% S and 26% carbon. Hulskotte et al. (2014) do not report measurements of Ba, but cite reported values of 0.07-6.9% from Spain and 12% from Japan. Correlations have been observed between Cu, Ba, and Fe observed in ambient particulate matter (Birmili et al., 2006) and with measurements at roadside (Gietl et al., 2010). Furthermore, using the robust ratio between Fe and Cu found at the kerbsides, a 70% and 30% estimate of the contribution of brake pads and brake discs (consisting almost entirely of metal with iron being the dominant element >95%) to total brake wear respectively was made.

Using data from roadside and local background locations, Gietl et al. (2010) estimated that barium comprises 1.1% of brake wear (PM_{10}) particles from the traffic fleet as a whole, allowing its use as a quantitative tracer of brake wear emissions at traffic-influenced sites. By using real time aerosol data, Dall´Osto et al. (2013) found that Fe and Cu together can also be used as a tracer of brake wear. Other studies have reported that the abrasion of brakes produces particles characterised by high concentrations of Cu, Ba, Zn and Fe (Sanders et al., 2003; Johansson et al., 2008). Iron is often considered to be related to crustal elements and resuspension of road dust (Sternbeck et al., 2002; Heal et al., 2005; Lough et al., 2005). However, Harrison et al. (2003) in devising a pragmatic mass closure method from analyses of particulate matter collected at UK sites, found that the iron

concentration within coarse dusts was much greater at roadside sites than at urban background sites and this was considered indicative of road traffic and most probably the vehicles themselves as a source. Birmili et al. (2006) confirmed that iron in coarse particles could be used as a tracer of vehicle-generated particles, whilst calcium is primarily a tracer of particles from soil, as also concluded by Harrison et al. (2003). Birmili et al. (2006), compared trace metal concentrations collected at four different measurement sites representing different degrees of traffic influence. The size-fractionated ambient PM analyses showed Fe, Ba and Cu correlated closely in the fraction $1.5 < D_p < 3.0$ μm in urban air. This finding supported the concept that most of these particles are not due to vehicle-induced resuspension but are directly emitted from abrasion processes.

Mass spectrometry of atmospheric aerosol has recently been established and has quickly become the most essential and fastest growing area of aerosol research (Laskin et al., 2012). Currently none of the available mass spectrometry instruments reaches ideality. For example, the Aerosol Mass Spectrometer (AMS) provides great quantitative information on limited number of chemical components (Jimenez et al, 2009), but does not analyse any species which does not volatilise at 600℃ (i.e. Se a salt, dust, Elemental carbon). The Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) provides information on many more chemical components (both refractory and non-refractory, size range 200-3000 nm) than the AMS, but the information is only semi-quantitative (Pratt and Prather 2012). However, the ATOFMS´ unique strength relies in the fact that it can monitor in real time variations in the single particle composition. Previous studies have indeed focused on the MS of different types of dust particles (Silva et al., 2000; Sullivan et al., 2007, 2009, Dall´Osto et al., 2010, 2014).

This paper extends such work by application of an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) to characterisation of brake wear particles in the size range between 0.3 and 3.0 µm. Mass spectral fingerprints of different dust particles have been determined and information at a single particle level is presented from both laboratory studies and from a number of different field studies in very different environments (at background, roadside and road tunnel sites). The ATOFMS results shown herein provide information on single dust particles at very high time resolution (minutes), hence allowing characterisation of the mixing state of brake wear particles, and comparison of their temporal trends with other dust particle types and meteorological conditions. We first report the characterization of single particle mass spectra of brake wear aerosol generated in the laboratory, with specific key m/z markers. We then report ambient data across a number of environments, and we discuss the differences encountered. Finally, correlations between different types of dust and traffic volume data are used to conclude the study.

2. EXPERIMENTAL

2.1 Instrumentation

This work reports the use of an Aerosol Time-of-Flight Mass Spectrometer (TSI ATOFMS 3800) for the study of brake dust particles. Since its introduction in the late 1990s, the ATOFMS has given valuable insights into the size and composition of individual airborne particles (Gard et al., 1997; Pratt and Prather, 2012). In essence, this instrument provides an aerodynamic diameter and a positive and negative mass spectrum for each particle ionised by a pulsed UV laser.

Two different versions of the ATOFMS are commercially available: ATOFMS TSI model 3800-100 and ATOFMS TSI Model 3800. In the ATOFMS TSI model 3800-100, particles are sampled through an orifice and accelerated through the aerodynamic lens to the sizing

region of the instrument (Su et al. 2004). By contrast, the ATOFMS TSI Model 3800 utilizes a nozzle/skimmer interface for the inlet (Gard et al. 1997). In terms of particle collection efficiency, the aerodynamic lens provides a major improvement toward smaller particle sizes compared to nozzle/skimmer inlet. Both instruments measure the aerodynamic diameter of particles sizes between 100 nm and 3 μm by calculating their time of flight between two orthogonally positioned continuous wave lasers (λ = 532 nm). However, a number of factors affecting the potential to extract fully quantitative information on particle size distributions - i.e. the transmission efficiency of the nozzle/skimmers used to create the particle beam in the instrument's inlet (Dall´Osto et al., 2006) - make the size responses of the two instruments quite different. Generally speaking, whilst the ATOFMS equipped with the lens provides mainly particles below 1 μm, the opposite case is found for the nozzle/skimmer inlet. Following the particle inlet and sizing part of the inlet, particles are then transmitted, in both TSI models (aerodynamic lens and nozzle/skimmer), into the mass spectrometry region of the instruments where the light scattered by the particles is used to trigger a pulsed high-power desorption and ionization laser (λ = 266 nm, about 1 mJ per pulse) that desorbs and ionizes the particle in the centre of the ion source of a bipolar reflectron ToF-MS. Thus, positive and negative ion spectra of a single particle are obtained.

Whilst the efficiency of the NI is heavily biased towards the super-micron aerosol (Gard et al., 1997), the AFL focuses a narrow particle beam for sizes between 100 nm and 3 μm (Su et al., 2004). Figure S1 compares the efficiencies of the two inlet types. Depending on the scientific objectives, past studies have typically used the AFL system to study ultrafine and fine anthropogenic emissions (Spencer et al., 2006) and the NI system has been used to study dust particles (Sullivan et al., 2007, 2009, Moffet et al., 2012). The combination of AFL and PMT pre-amplifiers increased the detection of particles (Hit Counts) of particles

with a diameter below 1.0 µm by a factor of 100. This is can be exemplified by comparing ambient data collected using the NI and the AFL with the PMT pre-amplifiers. The mode in the size distribution below 1.0 µm has greater amplitude for the AFL than the NI ATOFMS (Figure S3). Furthermore, when considering the size distribution of the brake dust cluster, the mode is not clearly present for the data collected using the NI ATOFMS.

It is important to note that a limitation of laser desorption/ionization (LDI) single particle mass spectrometry is that the process is heavily influenced by particle size, morphology and matrix composition, since these will influence energy transfer from the laser beam to the particle, vaporization of the particle and ion formation in the vaporization plume (Reilly et al., 2000; Schoolcraft et al., 2001).

Analyses of collected data were carried out using YAADA (Allen et al., 2001) run within the Matlab version 6.1 environment. The ART-2a neural network algorithm (Song et al., 1999) was used to reduce the complexity of each dataset by clustering particles into groups with similar mass spectral properties. ART-2a was applied using a learning rate of 0.05, vigilance factor 0.85 and a total number of 20 iterations. ART-2a generates a large number of clusters (in excess of 200) starting with those with a large number of particles, the main clusters, right down to the minor clusters which only have a few particles. The identity of the clusters is determined from the mass spectra and those from common sources are merged back together starting with the main clusters. Usually only the first 40-50 clusters are considered because those beyond 50 have too few mass spectra within them to be significant.

The data and clusters presented in this study have been collected in both laboratory and ambient field studies over a period (2001-2014) during which the ATOFMS inlet was

updated from using a nozzle (2001-2006), to an aerosol focussing lens inlet (2006-2014). In the update, the sensitivity of the ATOFMS to the smaller particles was increased by pre-amplifying the PMT light scattering signals and the analogue to digital converters used to read the ion signals from the micro channel plates were changed to increase dynamic range to stopping 'peak clipping'.

2.2 Characterisation of Brake Wear in Laboratory Studies

2.2.1 Brake wear ATOFMS nozzle orifice (NI) inlet laboratory study

In the early work using the nozzle inlet, brake dust ground from a brake pad was sampled into the ATOFMS. Mass spectra were obtained by placing each dust sample into a flask in a sonicator to create a suspension of dust particles under filtered lab air flow (Silva et al., 2000; Schofield, 2004). The aerosol was then directed into the ATOFMS inlet for analysis and about 1000 single-particle mass spectra were collected per sample. Due to the large range of brake pads used on vehicles and the limited information on composition, brake pads used on the ten best selling cars for 2001 in the United Kingdom (SMMT, 2002) were sampled using this method together with dust accumulated behind the wheel trim of a front wheel of a car (Schofield, 2004). The same methods have been applied in later studies (Sullivan et al., 2007, 2009; Dall´Osto et al., 2010).

2.2.1 Brake wear ATOFMS aerodynamic lens (AFL) inlet laboratory study

In later work using the AFL inlet, an automotive brake and calliper system was housed within a small enclosure. Brake dust was sampled from the enclosure directly by the ATOFMS. The disc was rotated by an electric motor and compressed air was used to force the brake pads onto the disc which was rotated at 1500 rpm corresponding to approximately 111 mph for a typical 65 cm diameter car wheel. Various brake pressures

(1-4 bar) were then applied which corresponded to light, medium and heavy braking raising the temperature of the back surface of the brake pad to over 60^{o}C.

2.3 Field Studies

2.3.1 Ambient field study using the nozzle inlet (NI)

During June and July 2002 the ATOFMS was deployed in Birmingham (UK). The aim of this work was to compare the composition of particles collected at each of three contrasting sites and to assess the application of the ATOFMS in source apportionment. Three different sites were chosen, each of which had differing degrees of traffic influence:

(i) The *Winterbourne* (WB) site, was an urban background site on the east side of the University of Birmingham campus (52°27'13"N; 01°55' 27"W). The location is within a residential area with the nearest road 100 m to the west and the busy A38 road, 500 m to the South. This urban background site was expected to be representative of the urban background PM on a scale of several km.

(ii) The *Queensway Underpass* (QW) site is part of the tunnel network that carries traffic to andfrom the M6 motorway under central Birmingham (52°28'47"N; 01°54'21"W). The tunnel is approximately 200 m long with the north-bound and south-bound lanes separated by a wall, with occasional gaps. The sampling site within the tunnel was in an emergency lay-by recessed into the walls of the bore for south-bound traffic. On travelling through the tunnel traffic is limited to 30 mph and has to take a left hand turn passing the sampling site before exiting the tunnel.

(iii) The *Bristol Road* (BR) site, is within the grounds of the University of Birmingham overlooking the busy A38 which is a major highway that runs from south-west to north-east through Birmingham (52°26'50"N; 01°55'42 "W). The traffic speed is again limited to 30 mph and the observatory was placed within 50 m of a traffic light controlled junction. The traffic volume at the roadside site was 22,000 vehicles per

day, with about 7% being heavy duty trucks and buses. Three campaigns were conducted at this site.

The ATOFMS was deployed in the three different locations for a total period of 17 days. Detailed information on starting time, sampling duration and total number of particles detected are given in Table 1.

2.3.2 Ambient field study using the aerodynamic lens (AFL) inlet

Following an upgrade in 2006, the NI inlet was replaced by the AFL system after which 3 subsequent field studies that were carried out at the following sites in London, Port Talbot and Barcelona:

(i) The *Marylebone Road* (MR) *site* is located on kerbside of a major arterial route within the city of Westminster in London (51°31'21"N; 00°0 9'17"W). This is on a heavily trafficked (ca. 80,000 vpd) six lane highway running through a street canyon in central London.

(ii) The *Port Talbot* (PT) *site* is located in the grounds of Margam Fire Station in South Wales located in South Wales (51°35'03"N; 03°46'16" W) 250 m away from the M4 motorway (ca 50,000 vpd). Port Talbot is a coastal industrial town with a population of approximately 35,000 and the Tata steelworks is the main industry area covering approximately 28 km^2, having a production capacity around 5 million tonnes per year.

(iii) The *Barcelona* (BCN) Road *site* (41°23'18"N; 02°09'00"E) was situated in a car par k of the Escuela de Ingeniería Técnica Industría (St. Urgell, 187 – elevation 40 m a.s.l.) next to C/ Urgell, a major highway composed of a one-way four lane road (17,000 vpd). With a population of about 1.7 million inhabitants in the city and around 4 million in the surrounding area, Barcelona is the fifth most populated metropolitan area in Europe.

Road dust samples were also collected between 8th October and 30th October from four different locations around London. The four sites were very different to each other and included a major road (Marylebone Road), a minor road (near the BT tower within the congestion zone), a road inside Regents Park (RP) and a footpath in Regents Park. At Marylebone Road, the samples were taken near Great Portland Street Underground station, and at the BT tower dust samples were collected on a corner between Cleveland Street and Maple Street. At the background sites, samples were taken on the Inner Circle of Regents Park which is a minor road on the inside of the park along which few vehicles (less than 50 per hour) drive. Leaves and soil can be often seen on the ground. Samples were also taken on a concrete/stone pedestrian footpath near York Bridge within the Park. For each location, the surface of the highway was brushed with a clean brush into a small plastic bag and a total of 46 samples were taken during the month of October 2006. The contents of the bags were then resuspended and analysed by ATOFMS yielding a total of 2791 single particle mass spectra which were grouped into 16 ART2a Road Dust clusters.

3. RESULTS

3.1 Laboratory Studies of Brake Dust

Art-2a was run on the 20,000 ATOFMS single particle mass spectra detected during the lab studies. The brake dust spectra sampled either via ‘a flask in a sonicator’ or an automotive brake and calliper system (ATOFMS nozzle and lens studies, respectively) were separated from the background and merged into one ATOFMS Art-2a brake dust cluster. The average mass spectra of the ATOFMS Art2a clusters of the two different ATOFMS inlets are shown in Figure 1.

The ATOFMS NI configuration spectra exhibit peaks from sodium ([^{23}Na]), aluminium ([^{27}Al]), potassium ([^{39}K]), iron ([^{56}Fe], [$^{\pm 72}$FeO], [$^{112}Fe_2$], [$^{128}Fe_2O$], [^{210}FeBaO], [$^{226}FeBaO_2$],

315 [$^{-88}FeO_2$] and [$^{-104}FeO_3$]), barium ([^{138}Ba], [^{154}BaO], [$^{210}FeBaO$], and [$^{226}FeBaO_2$]) although
316 only the more prominent peaks are seen in the average spectra of Figure 1. The negative
317 ATOFMS mass spectrum is mainly composed of elemental carbon peaks at m/z [^{-12}C], [$^{-}$
318 $^{36}C_3$], [$^{-48}C_4$], and [$^{-60}C_5$]. It is important to remember that the ATOFMS uses a 266 nm
319 wavelength for ionisation - and as such maybe biased towards the EC signature (due to
320 different absorption efficiencies and ionization potentials) - implying the ATOFMS will be
321 more sensitive to particles containing traces of EC relative to others containing OC.
322 Furthermore, copper peaks ([Cu], m/z 63 and 65) were seen in about 30% of the particles
323 analysed and interestingly some of the mass spectra indicated the presence of antimony
324 and its oxides in both positive and negative spectra ($[SbO_2]^{-}$, m/z +/- 153 and 155, $[SbO_4]^{-}$,
325 m/z -185 and -187).
326
327 The positive mass spectrum of brake wear material detected with the AFL inlet (Figure 1b)
328 was similar to that measured with the NI (Figure 1a), with the exception of the strong
329 presence of chlorides ([^{-35}Cl]), nitrates ([$^{-46}NO_2$] and [$^{-62}NO_3$]), and phosphates ([$^{-63}PO_2$]
330 and [$^{-79}PO_3$]) in the negative spectra. Barium peaks [Ba] and [BaO] (m/z 138 and 154)
331 were only observed using the nozzle inlet when comparing lab experiments. This
332 discrepancy can be explained by a difference in the available laser desorption energy
333 during the lab experiments and an energy threshold of 0.74 mJ for barium. The NI-
334 ATOFMS used 0.85 mJ whereas the AFL-ATOFMS used 0.19 mJ. Figure S4 plots the
335 percentage occurrence of [^{56}Fe], [$^{-88}FeO_2$] and [^{154}BaO] in the field data (discussed below)
336 as a function of laser energy and it is clear that [^{138}Ba] occurs only at higher energies
337 above 0.74 mJ. This later led us to understand - in the Field Studies section below - why
338 barium peaks were observed in the MR2009 and not the BCN2010 ambient data sets
339 (Figure 2). For MR2009 and BCN2010, the laser energies were 0.79 mJ and 0.74 mJ
340 respectively, above and below the threshold.

A dependence of the brake dust tracer peaks ([^{56}Fe] , [$^{-88}$FeO$_2$], [^{138}Ba] and [^{154}BaO] was also observed as a function of particle diameter (Figure S2). As the aerodynamic diameter of the brake dust particles increased to, and passed 1 µm, the fraction of [$^{-88}$FeO$_2$] and [^{138}Ba] and [^{154}BaO] detected increased. Again, [^{56}Fe] proves to be the most reliable tracer peak, being detected in 100% of the particles with aerodynamic diameters between 0.7 and 2.0 µm for both the NI and AFL. As for [$^{-88}$FeO$_2$], there was between 60% and 80% occurrence for particles greater than 0.9 µm detected using the NI and AFL. And similarly, for the [^{138}Ba] peak there was a 40% detection for both the NI and AFL, for particles of diameter greater than ~0.7 and ~1.2 µm respectively. Thus [^{56}Fe] and [$^{-88}$FeO$_2$] are more reliable markers for brake wear particles than [Ba] and [BaO] across all particle sizes. Furthermore, for the NI it was also realised that although soil particle spectra contained [^{56}Fe] peaks, [$^{-88}$FeO$_2$] peaks were observed very infrequently. According to Figure S2, at smaller particle sizes (<1 µm) there is a loss in sensitivity to the ions characteristic of brake dust. This may be due to in homogeneities in the brake dust particles, which would imply that the composition may vary within the sub-micrometre size range. The larger particles contain sufficient material that this effect is “averaged out”.

In summary, the characteristic features of brake wear particle types include intense [^{56}Fe] and [$^{-88}$FeO$_2$] signals, along with [^{138}Ba] and [^{154}BaO]. However, whilst the Ba marker is sensitive to the laser fluence, the Fe signals are not. Moreover, it is important to note that very few [$^{-88}$FeO$_2$] peaks are observed in other types of dust, including soil (Dall´Osto and Harrison, 2006), Saharan dust (Dall´Osto et al., 2010), Asian mineral dust (Moffet et al., 2012) and tyre dust (Dall´Osto et al., 2014). This iron cluster [$^{-88}$FeO$_2$],along with the strong presence of [^{138}Ba] is therefore a good indicator of brake dust particles.

3.2 Ambient Field Studies of Brake Dust

Five field studies were carried out in Birmingham UK, using the ATOFMS fitted with the nozzle inlet (Table 1) in which 201,746 mass spectra of particles were measured and subsequently classified into clusters using ART-2a. A number of mass spectra detected were similar to those shown in Figure 1a and apportioned to brake dust. The average brake dust mass spectrum detected in the Birmingham studies with the NI-ATOFMS is shown in Fig. 2a, clearly showing specific markers due to iron (m/z 56, m/z -88) and barium (m/z 138 and m/z 154). Other dust particle types were detected, including vegetative debris (5.2 % at BR2002 only, Table S1) and road dust (3.1-8.2 % across all 5 campaigns Table S1), but none of these contained the brake wear markers identified in this study.

Previous ATOFMS studies with NI-ATOFMS carried out in other locations have also reported this cluster. Dall'Osto et al. (2006) in Athens, Greece showed a cluster named 'car' - correlating with rush hour traffic - with strong signals at m/z 54, 56 and -88 due to iron [^{54}Fe], [^{56}Fe] and [$^{-88}FeO_2$], respectively). Peaks at m/z 138 and 154 are due to barium ([^{138}Ba] and [^{154}BaO]).

The average ATOFMS mass spectrum of particles attributed to brake dust collected attwo European sites with the AFL inlet is shown in Figures 2b and c. . The peaks are due to sodium ([^{23}Na]), aluminium ([^{27}Al]), potassium ([^{39}K]), iron ([^{56}Fe], [$^{\pm 72}$FeO], [$^{112}Fe_2$], [$^{128}Fe_2O$], [$^{-88}FeO_2$] and [$^{-104}FeO_3$]), barium ([^{138}Ba], [^{154}BaO], [^{210}FeBaO], and [$^{226}FeBaO_2$]), chlorides ([$^{-35}$Cl]), nitrates ([$^{-46}NO_2$] and [$^{-62}NO_3$]), and phosphates ([$^{-63}PO_2$]) and ([$^{-79}PO_3$]). These show similar tracer peaks of Fe, FeO_2^- and Ba although these are less frequently observed as the LDI laser energy decreased towards the Ba-LDI threshold.

Following the modification of the ATOFMS to use the AFL, brake wear particles were detected less often in urban field studies, and in some comparisons were not detected at all at background sites (Smith et al., 2012; Dall'Osto et al., 2009). Consequently we have a relatively low percentage of brake wear particles detected at MR2009 (1.0%), BCN2010 (0.3%) and PT2012 (~10%). Fe-rich particles associated with brake wear were detected at Marylebone Road (Figure 2) although Giorio et al. (2015) did not identify any Fe-rich particles in this Marylebone Road data set using the *k*-Means method. The clusters used in that study only accounted for 55% of the variance and when the spectral data base was queried, 1.5% of the dataset were identified as Fe-rich. Of these, 17% were attributed to brake wear, with spectra similar to those measured in the laboratory studies shown in Figure 1.

In the road dust samples, brake wear material was found only on the Marylebone Road and at very low percentages (2%). This is similar to the observation by Dall'Osto et al. (2014) which showed that tyre dust is a minor component of road dust, but unlike brake dust, tyre dust is internally mixed with the road dust as a result of the high adhesion forces resulting from the surface properties of the tyre rubber.

4. DISCUSSION

This study considers roadside and laboratory studies of brake dust emissions measured using an Aerosol Time-of-Flight Mass Spectrometer (TSI 3800 - ATOFMS). The results presented using the two possible inlet configurations (aerodynamic lens and nozzle inlet) show that brake dust particles are characterised by ion peaks at m/z [$^{-88}FeO_2$] and [^{138}Ba]] and have a size distribution with a modal diameter in the ATOFMS data of 1.5 µm aerodynamic diameter corresponding to an actual modal diameter of 1.3 µm after correction for inlet efficiency.

Table 1 includes a summary of the brake dust percentages detected at three urban sites in Birmingham UK during five different seasons spread over three years. The highest relative concentration of dust detected was at the tunnel site (QW2002), of which 60% of the total dust particles analysed were categorised as brake dust with the remaining dust particles being classified as road dust.

To our knowledge there are only a few studies which have reported brake wear material in urban environment at high time resolution. These includes ATOFMS studies (Gross et al., 2000; Dall'Osto and Harrison, 2006), and a recent PIXE paper (Dall'Osto et al., 2013) where a Fe-Cu particle type was reported at hourly time resolution. However, not only high time resolution but also high number counts are needed in order to draw meaningful conclusions on brake wear particles. The Queensway tunnel experiment gave us very high time resolution, but also a very high number of brake wear material particles. Indeed Figure 3a shows the temporal trend of these two types of dust (Brake and Road dust) detected at the tunnel site. There is a close, but not exact temporal correlation between both road dust and brake dust and the hourly vehicle count (Figure 3(a)). The slight differences between the times of the peaks may have arisen for a number of reasons. Traffic counts were taken for only 15 minutes of each hour and may not fully represent the entire hour. Also, there is no certainty of a constancy of the ventilation conditions of the tunnel, which along with source strength determine airborne concentrations. The vehicle fleet mix and driving mode may also have changed during the course of the day, thus influencing emissions. In comparison, at the roadside site, road dust correlated with Vegetative/Soil Dust ($r = 0.65$) (Figure 3b) and brake dust deviated from the trend showing a tendency to peak during the rush hour periods). The observation that brake dust particles are detected as a separate cluster to resuspended road dust, suggests that brake

dust is emitted directly into the atmosphere to be dispersed, with only a small amount settling into road dust. Alternatively, some may deposit to the road surface, but not be effectively resuspended.

Lough et al. (2005) reported that iron was the most abundant element in PM_{10} emitted in a road tunnel, and it was attributed mainly to brake wear emissions and resuspension of road dust. The size-resolved data for Fe presented correlate more closely with brake wear elements (Ba, Cu, Sb) rather than with crustal elements (Mg, Ca) which exhibit a coarser mode. Iron dominated the contribution of trace metals to total metal mass in all particle fractions ($PM_{2.5}$, $PM_{2.5-10}$ and PM_{10}) in a study conducted at Edinburgh (UK) (Heal et al., 2005). Both Birmili et al. (2006) and Harrison et al. (2003) reported that coarse Fe can be used as a tracer of vehicle-generated material. There are clearly important differences in the amount of Fe-related particles which arise from vehicle-induced resuspension and from the direct emission of abrasion products respectively

Aerosol emissions in road tunnels have been reported from several studies conducted in different locations. Sternbeck et al. (2002) reported that Cu, Zn, Cd, Sb, Ba and Pb were the most strongly enriched metals for which direct vehicle emissions are much more important than resuspension for their presence in the aerosol. On the other hand, Al, Ca, Ce, Fe, Mg, Mn and Ti were attributed to the resuspension of dust in the tunnels. However, it is important to note that the metal data reported by Sternbeck et al. (2002) were from the total particulate matter fraction. On the other hand, Gillies et al. (2001) reported that in the PM_{10} size fraction, the third most prominent species was iron, and apportioned a significantly greater mass to geological material, indicative of a substantial contribution from resuspended dust.

The mass spectral properties of other dust types (see Figure S5) serve to distinguish them clearly from the brake wear particles. In the Queensway tunnel (QW2002 site), most of the dust particles in the measured size range were due to brake dust and only a minor proportion to road dust. Sampling of particles from road surfaces in London for analysis by ATOFMS failed to detect particles characteristic of brake wear. Although measured in the ambient air, the brake dust cluster was not measured in dust samples swept from Regents Park, or a minor road (near the BT tower within the congestion zone). In fact, the cluster was only detected as 2% of the mass spectra generated from road dust samples swept from Marylebone Road. These particles are likely to be emitted by vehicles but it seems only a small percentage is deposited on the road and resuspended.

Birmili et al. (2006) found that in the same Queensway road tunnel, PM concentrations (< 0.5 µm) were enriched by a factor of 7.5, PM (1.5-3.0 µm) by a factor of 5.3 and PM (3.0-7.2 µm) by a factor of 2.6 compared to average urban background levels. The additional material is expected to originate from direct vehicle emissions.

Furthermore, time series collected in real time and in-situ show no association of brake wear particles with road dust and lead to the conclusion that the main proportion of brake dust in the $PM_{2.5}$ fraction is suspended directly from the braking system and dispersed in the atmosphere, with only a minor amount deposited on the road and resuspended. No conclusion can be drawn for the PM_{10} fraction, in which resuspension of Fe-rich dust particles is more likely to play an important role.

Regarding the other urban sites, the background site showed the smallest percentage of road dust particles, with only 3.1% of the particles sampled being of this type, and surprisingly no brake dust particles. At the roadside site, a lower proportion of dust

497 particles were detected during wintertime (BR2003; 8.7%; Table S1) than in the two field
498 studies conducted during the warmer months (BR2002 and BR2004, 25.2% and 20.3%,
499 respectively; Table S1). This is likely to be due to wet conditions during wintertime.
500
501 **5. CONCLUSIONS**
502 In earlier work (Dall'Osto et al., 2014) we have shown the power of the ATOFMS to identify
503 tyre dust particles in the atmosphere. This latest work characterises in detail the capability
504 of the ATOFMS to identify brake wear particles which inevitably include particles deriving
505 both from the brake pad/shoe and disc/drum. The most frequently observed characteristic
506 peaks in the ATOFMS mass-spectra of brake wear particles are [^{56}Fe] and [$^{-88}FeO_2$].. The
507 former peak is also frequently associated with other sources of iron such as soil dust but
508 the latter peak appears to be highly characteristic of brake wear. However, the presence
509 of peaks due to [^{138}Ba] and [^{154}BaO] is the strongest indicator for brake wear particles as
510 there few other sources of barium in the atmosphere but these appeared in the mass
511 spectra only at higher laser energies and it is recommended that individual instruments are
512 tested with brake wear samples to establish whether such peaks are visible at the laser
513 energies used. We show that we can separate brake wear dust from other types of dust,
514 mainly using the peak at mz -88. This peak is not seen in steel industry (Dall'Osto et al.,
515 2008) Asian (Sullivan et al., 2007; Moffett et al., 2012) or Saharan dust (Dall'Osto et al.,
516 2010).
517
518 Full quantification of brake wear particles in the atmosphere has not been attempted as
519 part of this study and would require a detailed characterisation of instrumental efficiencies
520 (inlet and ionisation) which was beyond the scope of the current work. Confirmation of the
521 use of barium as a marker element for brake wear particles supports the approach used by
522 Gietl et al. (2010) of estimating brake wear particle concentrations from airborne

concentrations of this element. It should, however, be noted that brake wear composition varies from country to country and is subject to change with time. Consequently any method applied to the quantification of brake dust particles in the atmosphere including the ATOFMS would need to be calibrated against local conditions before the data were used for quantification purposes. Nevertheless, we show that brake wear particles generated in the laboratory and in the ambient air are very similar (contrary to tyre dust which interacts with road surface material). In addition, we see that brake wear is a source of iron that is likely to be from a different iron source to dust road and other mineral dust.

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TABLE LEGEND

Table1: ATOFMS field studies conducted using the Aerodynamic Focussing Lens (AFL) and Nozzle Inlet (NI).

FIGURE LEGENDS

Figure 1: Average mass spectra of laboratory brake dust particle clusters derived from ART2a using the nozzle inlet and 0.85 mJ laser energy (*left panels*) and AFL inlet and 0.19 mJ laser energy (*right panels*). The top graphs show ion current expressed as an absolute area of the peak. The lower graphs show the fraction of particles having the specified m/z peak.

Figure 2: Average mass spectra of ambient brake dust particle clusters derived from ART2a using the nozzle inlet (*left panels* and 0.82 mJ laser energy *BHAM2002)* and AFL inlet (middle panels and 0.79 mJ laser energy *MR2009 and right panels* 0.74 mJ *BCN2010*). The upper and lower panels are generated as in Figure 1 and *BHAM2002* represents the average of *BR2002* and *QW2002*.

Figure 3: **(a)** Temporal trend of unscaled ATOFMS counts for brake dust and road dust along with number of vehicles detected during the Tunnel experiment (hourly resolution); **(b)** Time series of three dust types.

Table 1: ATOFMS field studies conducted using the Aerodynamic Focussing Lens (AFL) and Nozzle Inlet (NI).

	Nozzle ATOFMS					Aerodynamic lens ATOFMS		
Campaign	*WB2002*	*BR2002*	*BR2003*	*BR2004*	*QW2002*	*MR2009*	*BCN2010*	*PT2012*
Site Type	background	roadside	roadside	roadside	tunnel	roadside	roadside	Industrial
Period	25-28/06/2002	08-12/07/2002	09-15/12/2003	25-29/05/2004	02/07/2002 05:00-20:00	22-05-2009 11-06-2009	16-09-2010 16-10-2010	18-04-2012 16-05-2012
Laser DI Energy (mJ)	----------	----------	0.82	----------	----------	0.79	0.74	0.49
N^{o}. of mass spectra (per day)	18,359 (6,120)	35,763 (8,941)	67,943 (1,132)	68,709 (17,177)	10,972 (17,555)	684,644 (34,232)	890,873 (29,696)	537,593 (19,200)
N^{o}. of brake mass spectra (per day)	-	5364 (1341)	2650 (442)	5772 (1,443)	6583 (10,533)	6846 (342)	2673 (89)	2150 (78)
Total n^{o}. clusters	10	15	19	16	7	14	18	18†
Brake dust as a percentage of dust mass spectra	-	15	3.9	8.4	60	1.0	0.3	0.4

† Analysed using *k*-Means in Enchillada (Gross et al., 2000; Giorio et al., 2012).

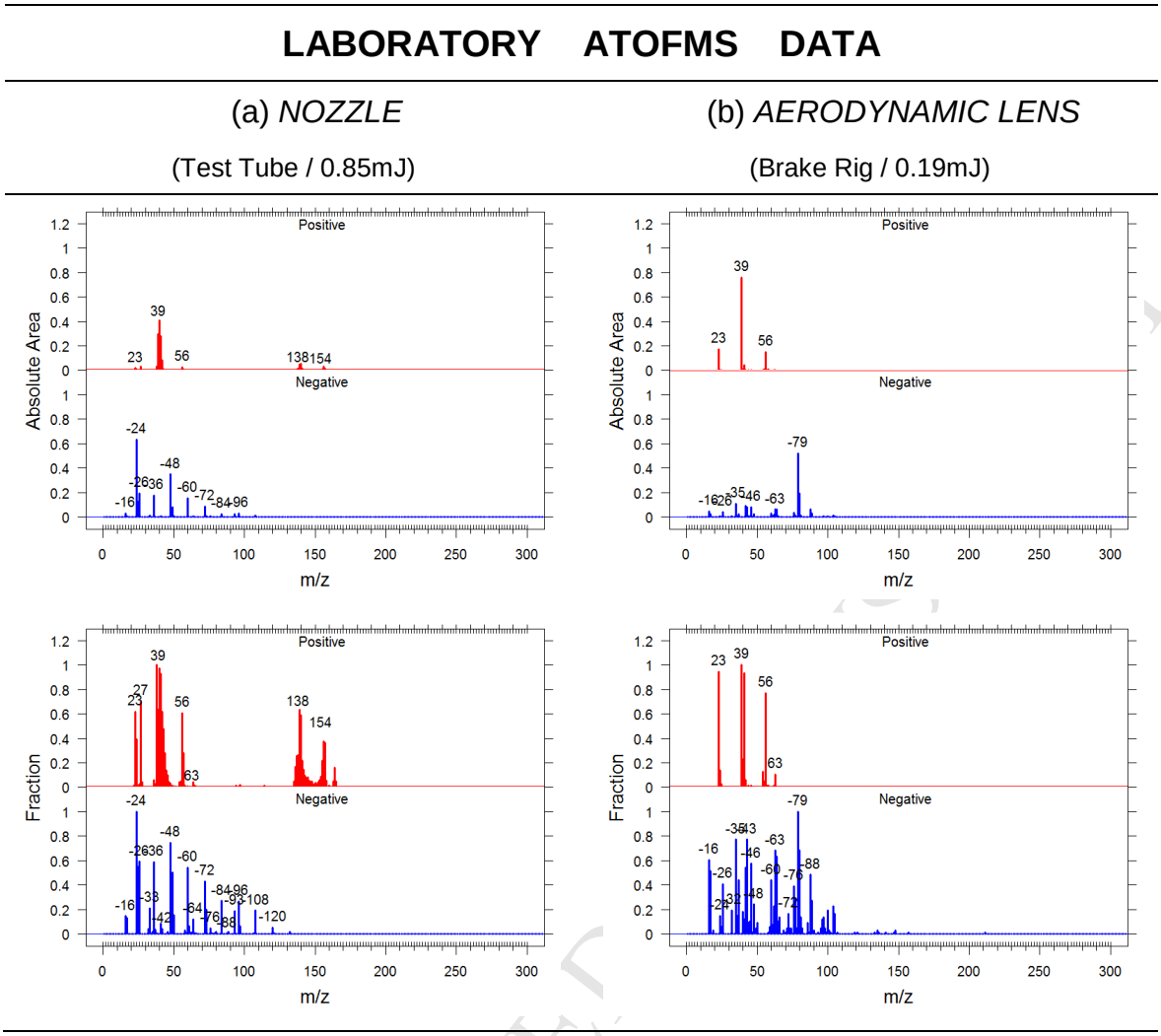


Figure 1: Average mass spectra of laboratory brake dust particle clusters derived from ART2a using the nozzle inlet and 0.85 mJ laser energy (*left panels*) and AFL inlet and 0.19 mJ laser energy (*right panels*). The top graphs show ion current expressed as an absolute area of the peak. The lower graphs show the fraction of particles having the specified m/z peak.

AMBIENT AIR ATOFMS DATA

(a) *BHAM2002 / NI* (b) *MR2009 / AFL* (c) *BCN 2010 / AFL*

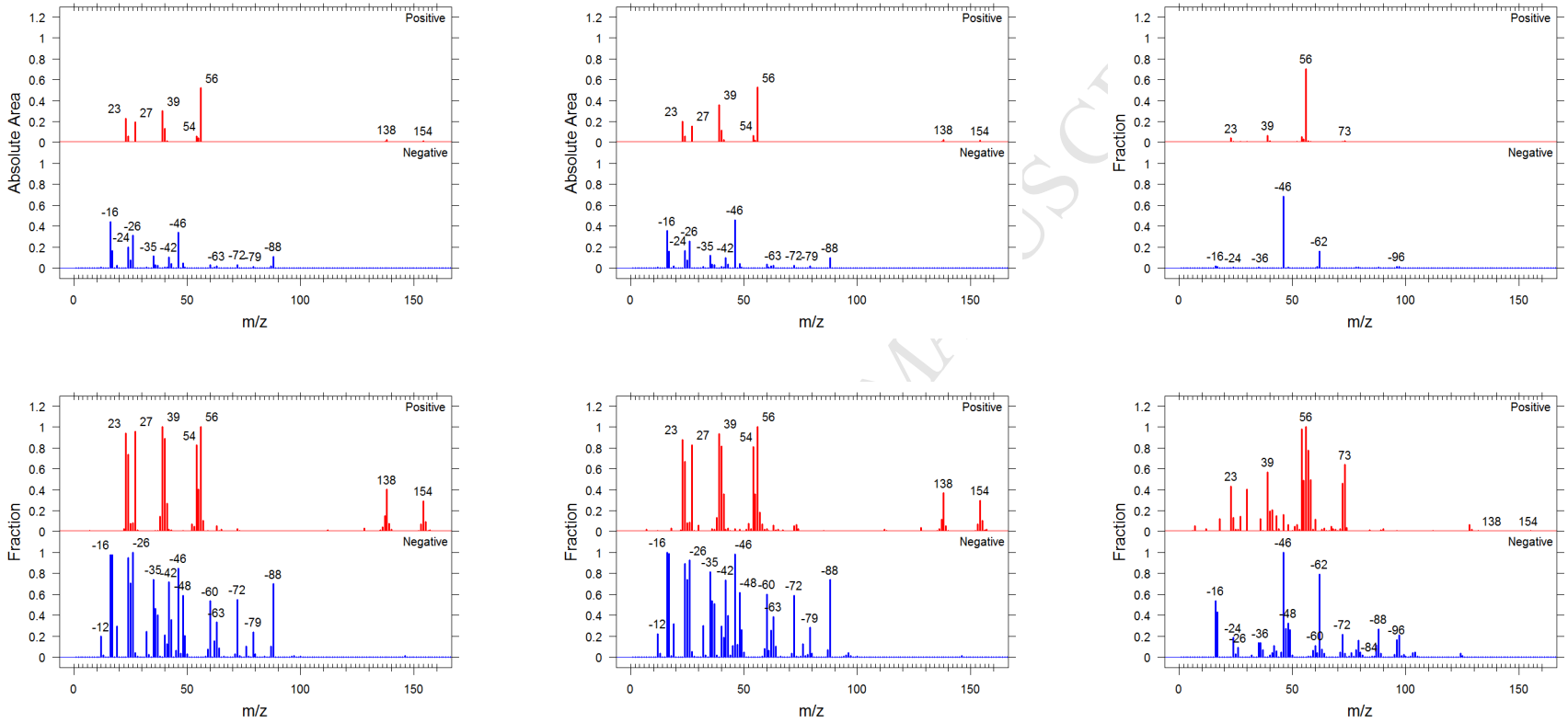
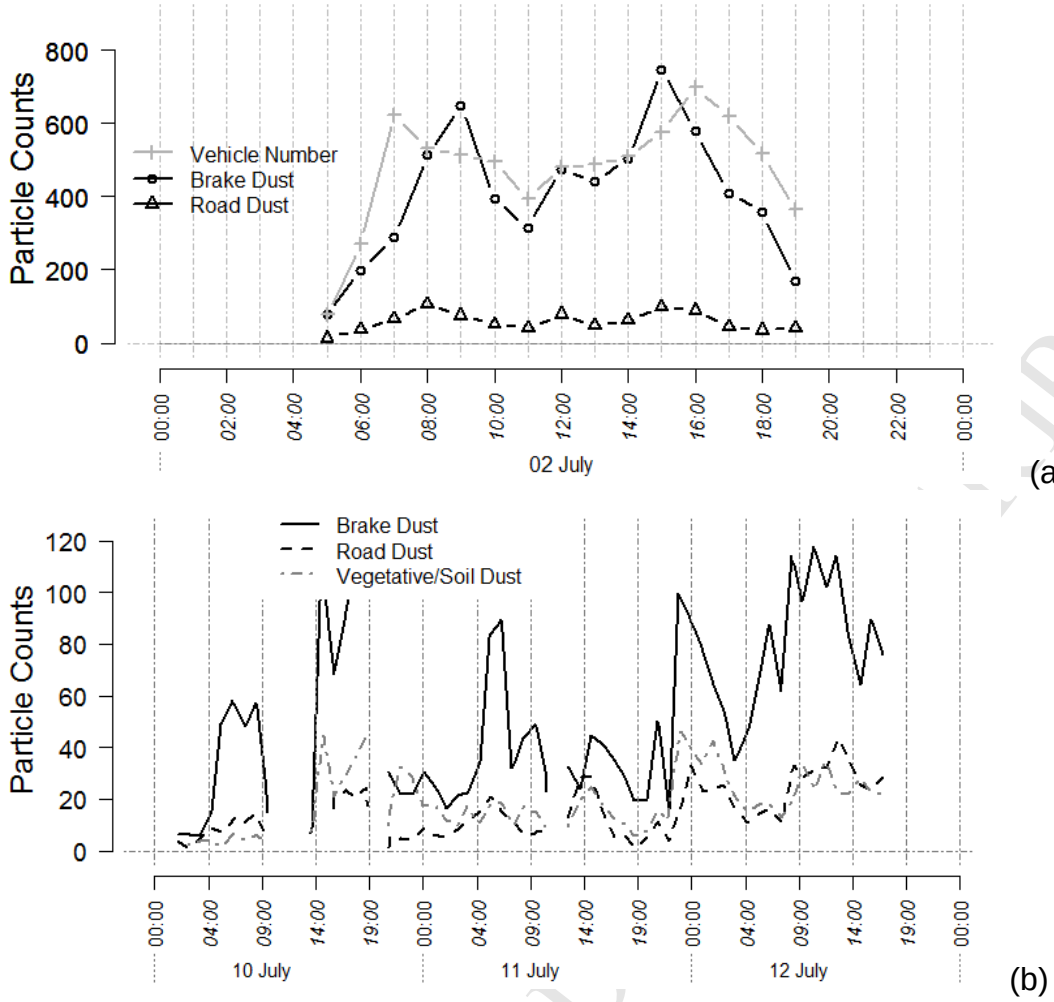


Figure 2: Average mass spectra of ambient brake dust particle clusters derived from ART2a using the nozzle inlet (*left panels* and 0.82 mJ laser energy *BHAM2002)* and AFL inlet (middle panels and 0.79 mJ laser energy *MR2009 and right panels* 0.74 mJ *BCN2010*). The upper and lower panels are generated as in Figure 1 and *BHAM2002* represents the average of *BR2002* and *QW2002*



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